**MS02.03.05 INTENSITY STATISTICS AND DIRECT METHODS FOR INCOMMENSURATELY MODULATED CRYSTALS.** Erwin J. W. Lam (Crystallography Laboratory, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands)

The application of direct-methods procedures for structure analysis to incommensurately modulated crystals is by no means trivial because, due to atomic modulations, the X-ray diffraction intensities of these crystals show different statistical behavior when compared to nonmodulated crystals. This is especially true for the satellite reflections. Although a study by Hao et al. (1987) showed that the Sayre equation can be applied successfully to X-ray diffraction data of incommensurately modulated crystals, this procedure employed structure factors (F) instead of normalized structure factors (E) because a definition of the latter was not at hand at the time.

It was shown by Lam et al. (1992, 1994) that average X-ray diffraction intensities for modulated crystals can be estimated from a Wilson-like plot in which the atomic modulations are taken into account by introducing overall modulation amplitudes. E values calculated from these average intensities were shown to be applicable in direct-methods procedures using the triplet-phase relation or the Hughes-Sayre equation (de Gelder et al., 1996).

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Hao, Q., Liu, Y.-W. & Fan, H.-F. (1987). *Acta Cryst.* A43, 820-824.
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**MS02.03.06 PHASE DETERMINATION AND EXTENSION USING X-RAY MULTIPLE DIFFRACTION AND MAXIMUM ENTROPY METHOD.** Shih-Lin Chang*# and Chien-Mei Wang*, *Department of Physics, National Tsing Hua University, Hsinchu 30043, Taiwan, R.O.C., #Synchrotron Radiation Research Center, Hsinchu 30077, Taiwan, R.O.C.

We develop a new scheme which combines the multiple diffraction technique with the maximum entropy method so as to extend the phases of structure factors and solve the current phase problem. In this approach, we use the known structure of the organic crystal $C_{25}H_{25}NO_2$ as the example. The organic crystal has four molecules(Z=4) in a unit cell and belongs to the space group $P2_12_12$, orthorhombic, with the cell dimensions 20.30 x 14.86 x 6.98Å$^3$. We experimentally determined 77 individual phases from 90 experimental triplet phases calculated from 215 measured psi-scan 3-beam and 4-beam diffraction profiles obtained with a rotating-anode x-ray source and synchrotron radiation, where the psi-scans were around the reciprocal lattice vectors of the (001), (002), and (003) reflections.The experimentally determined individual phase, used as the starting phases , are treated as the input to the process of estimating the values of probable structure factors, both magnitudes and phases, via the optimization of the entropy. Based on this electron density distribution, we refine the phases related to the experimentally determined individual phases with the maximum entropy method constrained by the triplet phases.With this approach,we have so far succeeded in phase extension up to more than a hundred reflections.

**MS02.03.07 ON THE EXPANSION OF KARLE-HAUPTMAN DETERMINANTS INTO MULTIPLETS AND THE MAXIMUM ENTROPY RULE.** Oscar E. Piro,[1] C. de Rango,[2] G. Tsoucaris[2] and G. Navaza[2], [1]Dept. Fisica, Ftad. C. Exactas, Univ. Nacional de La Plata, C.C. 67, 1900 La Plata, Argentina, [2]Laboratoire de Physique, Faculte de Pharmacie, Universite de Paris-Sud 92290 Chatenay-Malabry, France

Improved Direct Methods formulations employing besides triplets, quartet and quintet products of structure factors (phase invariants) clearly suggest the useful phase information conveyed by higher-order multiplets in structure determination procedures. These formulations can be obtained from the first few terms in the expansion of large joint probability distribution (j.p.d.) of structure factors constructed on the basis of K-H determinants, combined with the reciprocal space Maximum Entropy rule. In this connection, it has been pointed out that the power of current Direct Methods to solve large crystal structures is limited by the usual practice of approximating large j.p.d.'s by piecing together marginal distributions of single invariants. It is therefore interesting to describe how the full phasing power of large j.p.d.'s is reached by the progressive incorporation of phase information due to higher-order multiplets. As a contribution to this goal, we disclose herewith the group theoretical structure of the contributing phase invariants in the expansion of an arbitrary m-order K-H determinant into multiplets up to the order m. Implications and possible applications of the results will be discussed.

**MS02.03.08 DISCRETE HILBERT TRANSFORMS AND THE PHASE PROBLEM IN CRYSTALLOGRAPHY.** A.F.Mishnev. S.V.Belyakov, Latvian Institute of Organic Synthesis, Riga, Latvia.

On the analogy to the optical image reconstruction theory the role of in-between structure factors (having half-integral Miller indices) has been investigated in application to the crystallographic phase problem. Relation between normal (having integral Miller indices) and in-between structure factors (SF) is given by the discrete Hilbert transforms (DHT)

$$F(h'/2, k'/2, l'/2) = (1/j) \sum_{h,k,l}{}' F(h/2, k/2, l/2)\left[1-(-1)^{h'-h}\right]/\left[\pi(h'-h)\right] \quad (1)$$

$$\times \left[1-(-1)^{k'-k}\right]/\left[\pi(k'-k)\right]\left[1-(-1)^{l'-l}\right]/\left[\pi(l'-l)\right],$$

where the prime on the summation sign indicates that terms with h=h', k=k' and l=l' are omitted, j=$\sqrt{-1}$ . When h',k',l' in the left-hand side of(1) are odd, than in the right-hand side terms with h, k, l odd will cancel and (1) will give the values of in-between SF in terms of normal ones. In-between SF can be incorporated into the phasing process by means of the autocorrelation function (ACF, Patterson for a single unit cell), which has the following form

$$A(u,v,w) = (1/8V) \sum_{h,k,l} I(h/2, k/2, l/2) \cos\pi(hu+kv+lw) \quad (2)$$

Formula (2) contains both normal and in-between intensities, which can be calculated from normal SF using (1). When the causal Fourier transform condition (Fourier transform vanishes for negative arguments) is satisfied for projections of the ACF, DHT applied to intensity function provide intensity oversampling at in-between points as follows

$$I(h'+1/2, k'+1/2, L) = -(1/\pi^2) \sum_{h,k} I(h,k,L)/[(h'-h+1/2)(k'-k+1/2)]. \quad (3)$$

Properties of the ACF (non-negativity, boundedness in space and magnitude) and its relation to the Patterson function give rise to new criterions for the correctness of phase sets. Phase refinement procedures based on minimum-negativity constraint and fitting of ACF to Patterson are suggested.